Synthesis and Properties of HVPE Nitride Substrates

R. P. Vaudo, G. R. Brandes, M. F. Chriss, C. S. Christos, J. S. Flynn, D. M. Keogh, F. D. Tamweber, X. Xu
ATMI, Inc.
7 Commerce Dr., Danbury, CT, 06810

The lack of a native nitride substrate is a major barrier to achieving the full potential of devices made from the III-V nitrides. The high density of defects in epitaxial material grown on foreign substrates inhibits the development and limits the performance of high power, high frequency electronic devices and short wavelength optoelectronic devices. The thermal coefficient of expansion (TCE) mismatch between the device layer and the non-native (foreign) substrate causes cracking and other strain-alleviating defects. Furthermore, non-corresponding cleavage planes complicate the cleavability of GaN-based films on foreign substrates and the electrical characteristics of foreign substrates are not readily modified. Efforts to make bulk GaN substrates by conventional techniques are restricted by the large vapor pressure of nitrogen at elevated temperatures.[1] Although lateral epitaxial overgrowth (LEO) material enables a marked reduction in the defect density of GaN grown immediately above the SiO_2 mask,[2] highly defective regions between low defect density mesas limit the applicability of this approach as currently implemented. In this presentation, we will discuss a vapor phase-based approach to solving these problems through the production of free standing GaN substrates and we will discuss the properties of the freestanding GaN, epitaxy on the GaN, and the performance of LEDs fabricated on sapphire and free standing GaN.

Hydride vapor phase epitaxy (HVPE) was used to produce GaN substrates of high crystalline quality. Briefly, GaCl, formed by flowing HCl over liquid Ga, ammonia and a dopant gas (e.g. silane) were introduced into a reactor in which the substrate and surrounding surfaces are at temperatures in the range of 900-1100 °C. The GaCl and ammonia reacted at the surface of the substrate to produce GaN, HCL and H_2. We obtained growth rates in the range of 15-150 μm hr^{-1} and sapphire and Si growth templates were used. To produce free-standing GaN, the growth template may be removed by destruction of the template (etching or grinding) or by parting the GaN substrate through decomposition of an interface layer (etching or optical). Figure 1 shows free-standing GaN produced by irradiating through the sapphire the interface region using 355nm light produced from tripling the output from a Nd: YAG laser.[3] The light was absorbed within 100nm of the interface and caused the GaN nitride to decompose. To reduce damage during parting, the sample was heated to >500 °C. To produce a suitable substrate the GaN is then sized and polished.

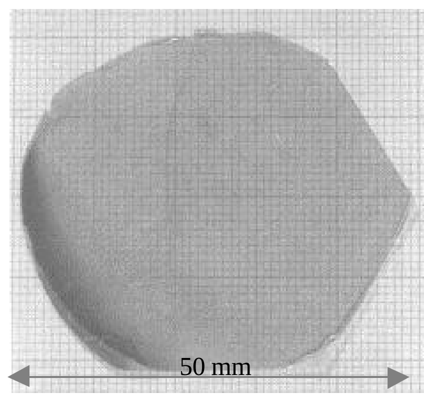


Figure 1. Low magnification optical photograph of freestanding GaN. The GaN is 250 μm thick and the crack-free right hand piece measures ~970 mm^2 in area. Note small grid elements are 1 mm^2.

The XRD-measured crystalline quality and the TEM-measured defect density improved with distance from the growth template in the GaN grown by HVPE. For example, when growing on sapphire we observed at the sapphire-GaN interface a threading dislocation (TD) density of $>10^{10}$ cm^{-2}. Ten microns from the interface, the TD density was reduced to 10^9 cm^{-2}. At a distance 300 μm from the interface, we observed a dislocation density as low as 3×10^6 cm^{-2} as measured with plan view TEM.[4] Similarly, the donor concentration and impurity concentration (SIMS) decreased dramatically with film thickness. For example, we measured $N_d=10^{20}$ cm^{-3} 0.1μm from the interface and N_d as low as 3 x 10^{15} cm^{-3} for distances of 300 μm from the interface. The carrier concentration was made to increase by introducing silane into the reactor during growth. Silicon was found to incorporate in proportion to the silane partial pressure and carrier concentrations as high as 10^{19} cm^{-2} were achieved. The thermal conductivity in the high crystalline quality GaN substrates was also measured. As

[1] S. Porowski, *et al*., Mat. Res. Soc. Symp. Proc. **449** (1997) 35.
[2] O.H. Nam, M.D. Bremser, T.S. Sheleva, R.F.Davis, Appl Phys. Lett. **71** (1997) 2638.
[3] M. K. Kelly, *et al.,* Jpn. J. Appl. Phys. **38** (1999) L217.
[4] R.P. Vaudo, *et al*., ICNS 1997.

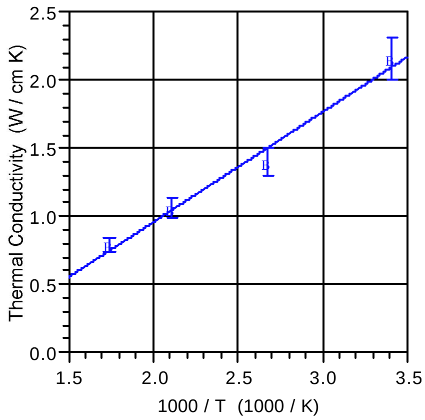


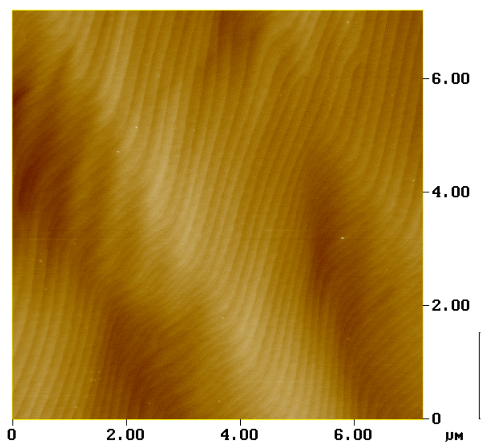
Figure 2. Thermal conductivity of GaN substrate as a function of temperature.

shown in Figure 2, we obtained a thermal conductivity of 2.2 ± 0.2 W cm^{-1} K^{-1} at room temperature with predictable decrease in thermal conductivity with increasing temperature.

Homoepitaxial films were grown by MOVPE on the GaN substrates. As shown in Figure 3a, smooth, gradually stepped homoepitaxial films were achieved without the need for a nucleation layer. The RMS roughness of the film shown in Figure 3a was 0.6 nm. Cross sectional TEM and SIMS studies showed no increase in the defect density and no increase in the impurity concentration in the interface region.

Identical light emitting diodes structures were grown for comparison on 3 different substrates – (i) sapphire with an AlN buffer layer, (ii)10 µm thick HVPE GaN on sapphire and (iii) undoped, freestanding GaN substrates. The epilayer structures consisted of 1.2 µm GaN:Si ($N_d=10^{18}$ cm^{-3}), 0.1 µm InGaN and 0.25 µm GaN:Mg ($N_a \approx 5\times10^{17}$ cm^{-3}). Following RIE etching, Ti/Al contacts were made to the GaN:Si layer and Ni/Au contacts were made to GaN:Mg layer. The contacts were annealed to 425 °C under forming gas prior to measurement.

(a)



(b)

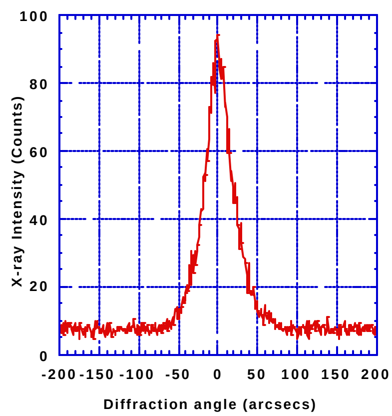


Figure 3 (a) AFM scan of homoepitaxial film grown by MOVPE on unpolished HVPE GaN substrate. **(b)** DCXRD scan of film shown in (a).

We observed greater than a four-fold increase in the output power for LEDs formed on the low defect density GaN substrate compared to LEDs formed on the other two substrates. Figure 4 shows the EL relative intensity of the LED formed on the free standing GaN substrate at two different currents. The forward voltage of the LEDs formed on the GaN substrates averaged 4.5V and the output power increased linearly with current over the range from 10-50mA. The LEDs are being packaged so that meaningful comparisons of the output power to commercially available LEDs may be made.

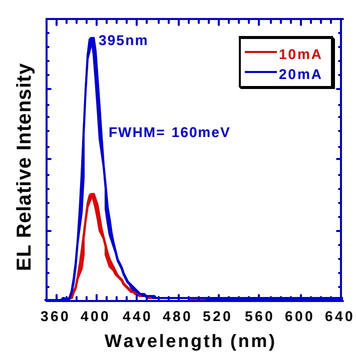


Figure 4. Electroluminescence of LED fabricated on GaN substrate.

In conclusion, GaN substrates of high crystalline quality were made using HVPE. The freestanding GaN substrates enabled the growth of high crystalline quality epitaxial layers and a significant increase in the performance of LEDs formed on them. Further characteristics of the substrates, epitaxial films and devices will be presented. We gratefully acknowledge the support of BMDO (DASG60-00-C-0036).